TITLE IMPROVED IRON CATALYSTS FOR SLURRY PHASE FISCHER-TROPSCH SYNTHESIS

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## ABSTRACT

## OBJECTIVES

The main objective of this project is to develop improved attrition resistant iron catalysts for converting coal-derived synthesis gas to high quality diesel fuels in slurry reactors. Slurry phase catalysts based on iron tend to break down into fine particles leading to severe operational difficulties in separating the hydrocarbon products from the catalyst. Attrition resistant catalysts will be prepared by spray drying in a bench-scale spray drier unit. Attrition behavior will be studied in a stirred tank reactor (STSR) by determining particle size distribution at the start of the test (TOS = 0) and at the end of the run (EOR). This provides a direct measure of changes in particle size distribution in the STSR during F-T synthesis, and accounts for both physical and chemical effects. The attrition resistance and the catalyst performance during F-T synthesis will be determined simultaneously under conditions representative of industrial practice.

## RECENT ACCOMPLISHMENTS

We have prepared several iron F-T catalysts by spray drying in two bench scale spray dryer units manufactured by APV and located in Food and Protein Research Center at Texas A&M University. Most experiments were conducted in a smaller unit (APV Anhydro Lab S1), 1 m in diameter and 2.4 m

in height. A limited number of experiments were made in a larger unit (APV Anhydro), 2.1 m in diameter and 2.4 m in height. Spray-dried catalysts were prepared from several different precursors. We prepared several catalysts starting from vacuum dried precursors (Fe/Cu/K/$SiO_2$, $SiO_2$ from potassium silicate), followed by sieving and milling to particles less than 5 μm in diameter, and then mixing them with water to form a slurry. The other procedures utilized a wet catalyst precursor (Fe/Cu or Fe/Cu/$SiO_2$), which was sonicated in an ultrasonic bath and then spray-dried. Catalysts of the same nominal composition 100 Fe/3 Cu/5 K/16 $SiO_2$ (in parts by weight) were prepared using different types (sources) of silica, i.e. potassium silicate, colloidal silica or tetraethyl orthosilicate (TEOS). Morphology and approximate size distribution were determined by scanning electron microscopy (SEM). It was found that particles prepared from vacuum dried precursors were irregularly shaped, except for small particles (~5-10 μm in diameter), which were nearly spherical. Spray-dried catalysts, prepared from wet precursors were spherical with smooth surfaces. The particle size distribution was fairly broad ranging from 5 μm to 40 μm in diameter (from SEM micrographs).

Both precipitated and spray-dried catalysts were tested in a 1 liter stirred tank slurry reactor (Autoclave Engineers) at 260°C, 1.5 - 2.2 MPa, 4-6 Nl/g-Fe/h using coal derived syngas feed ($H_2/CO = 0.67$). Test duration was between 170 and 500 h on stream. During testing at baseline process conditions (1.5 MPa and 4 Nl/g-Fe/h) the performance of spray-dried catalysts prepared from wet precursors was similar to that of precipitated TAMU's catalyst of the same composition. Syngas conversion was high (72-76%) and the catalysts had excellent selectivity characterized by low methane yield (2.6-3% on carbon atom basis) and high yield of liquid and wax hydrocarbon products ($C_5^+$ = 78-82%).

Attrition properties of eight iron F-T catalysts tested in the STSR under F-T reaction conditions for 300-500 h were determined from SEM micrographs and particle size distribution (PSD) measurements (Coulter Counter Multisizer). Catalyst samples suspended in hydrocarbon wax (or initial startup fluid) were withdrawn from the STSR, and then thoroughly washed with a mineral spirit (Varsol) to remove residual wax (initial fluid) before SEM and PSD measurements. Particle size reduction was observed in all tests, but attrition effects were not severe for seven of the eight catalysts tested. For these seven catalysts the relative percent change in the volume moment diameter (defined as: % of change = [(VMD (TOS = 0) – VMD (EOR))/(VMD (TOS = 0))] * 100) between 3.6 and 18.6%, whereas the increase in fraction of particles smaller than 10 μm in diameter was between 0.7 and 7.8%. In other words both particle fracture and erosion were relatively small. All these catalysts should be suitable for use in slurry bubble column reactors, where physical attrition is expected to be less severe than in the STSR.

The catalysts synthesized at TAMU have high attrition strength, and are very active and selective for production of liquid fuels from coal-derived synthesis gas. Two iron F-T catalysts prepared at Hampton University also have high attrition strength and excellent selectivity to liquid hydrocarbons, but their stability needs to be improved.

## ARTICLES, PRESENTATIONS AND STUDENT SUPPORT

Bukur, D. B. and Sivaraj, C., "Supported Iron Catalysts for Slurry Phase Fischer-Tropsch Synthesis", Applied Catalysis A, 231, 201-214 (2002).

Pham, H. N., Nowicki, L., Xu, J., Datye, A. K., Bukur, D. B. and Bartholomew, C., "Attrition Resistance of Supports for Iron Fischer-Tropsch Catalysts", submitted to I&ECR.

### Conference Presentations

Dragomir B. Bukur, Ketil F. Hanssen and Chokkaram Sivaraj, "Supported Iron Catalysts for Fischer-Tropsch Synthesis", paper presented at the AICHE Spring National meeting, April 2001, Houston, Texas.

Dragomir B. Bukur, Wen-Ping Ma, Victor H. Carreto Vazquez, Lech Nowicki and Adeyinka A. Adeyiga, " Spray Dried Iron Catalysts for Slurry Phase Fischer-Tropsch Synthesis", paper to be presented at the 226$^{th}$ ACS National meeting, September, 2003, New York City, New York.

Dragomir B. Bukur, Lech Nowicki, Abhaya K. Datye and Hien N. Pham, "Attrition Resistant Iron Catalysts for Synthesis Gas Conversion to Liquid Fuels", paper to be presented at the AICHE National meeting, November 2003, San Francisco, California.

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Mr. Victor Carreto-Vazquez (M. Sc. Student) – Contributions: catalyst synthesis and spray drying, characterization by SEM, and PSD measurements.

Mr. Jian Wang (Ph. D. Student) –catalyst testing in a STSR.

Dr. Wen-Ping Ma (post-doctoral fellow) has been primarily responsible for catalyst testing in slurry reactors.